



Infrared Spectroscopy

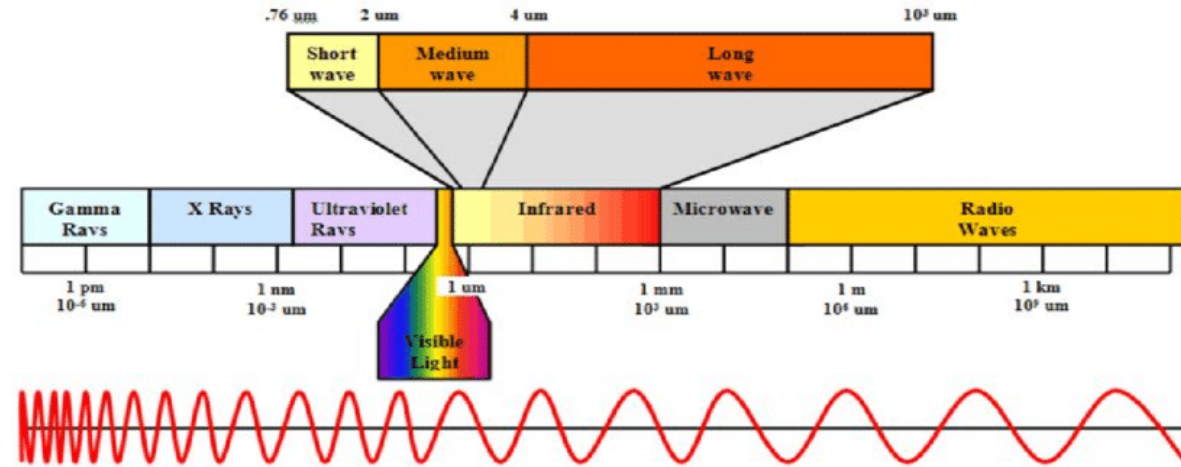
Fasiha Israr & Lisa Riedlsperger

Principle



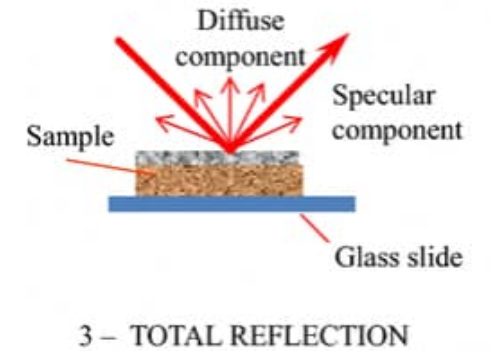
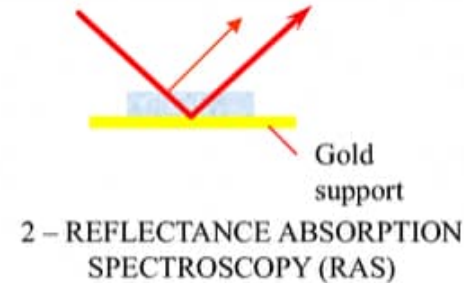
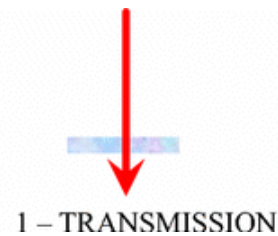
The IR spectrum
Between Visible and Microwave
Divided into

- Near-infrared – changes in crystal structure
- Mid-infrared – functional groups in organic molecules and crystal lattice changes
- Far-infrared – analyze lattice vibration (minerals and inorganic material)



IR spectroscopy modes

- Transmission
- Reflectance Absorption
- Total Reflection



Principle

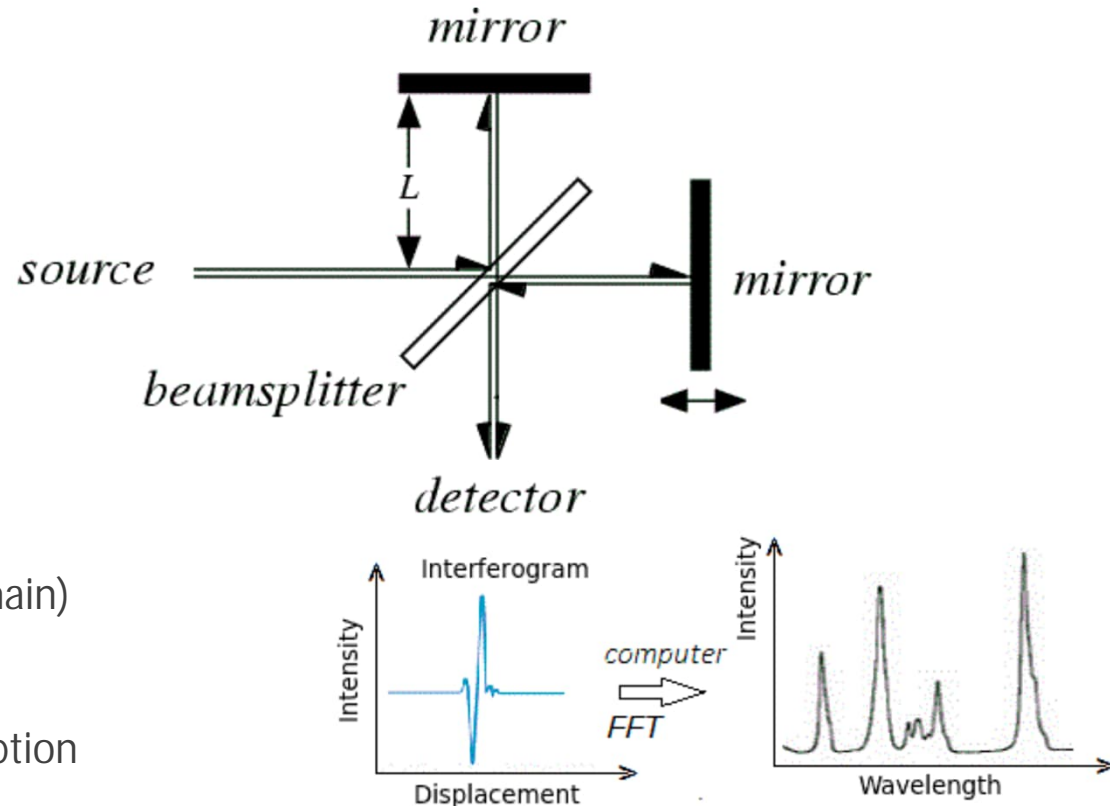


The Set-up
Reference and sample beams
Moving mirror

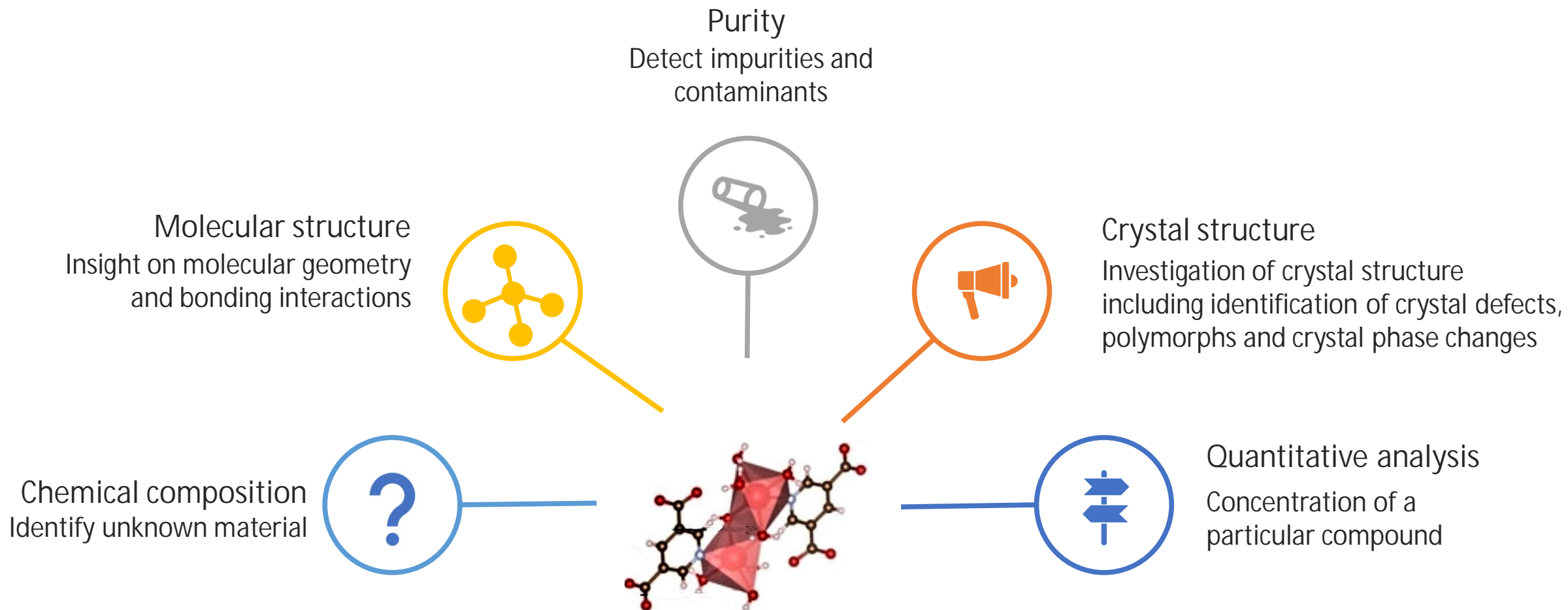


Fourier Transformation

- Transformation of the data (time domain) to the frequency domain
- Spectrum shows Transmission/Absorption of radiation by sample and is like a fingerprint

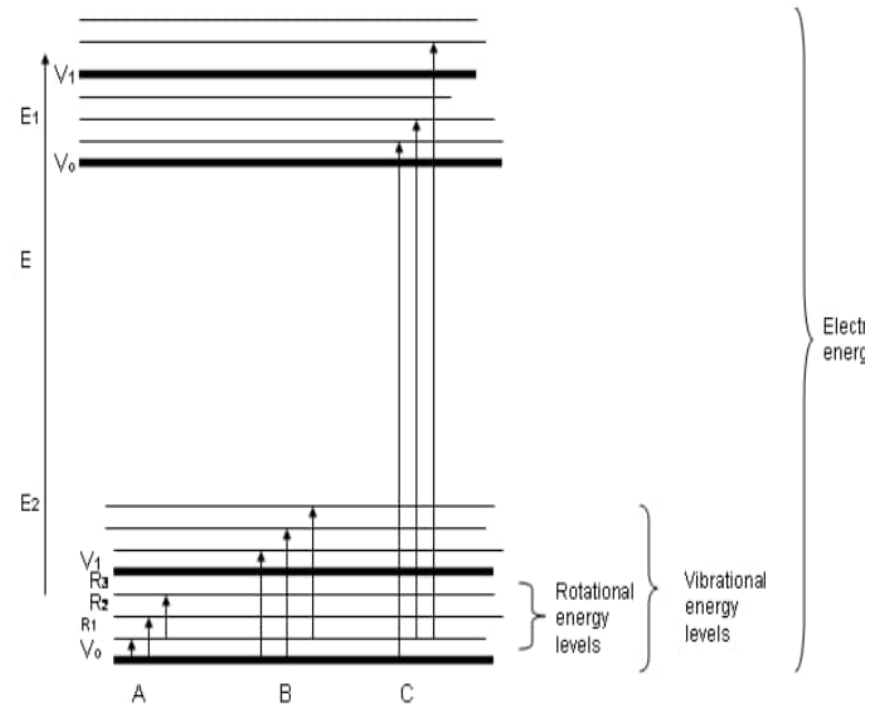
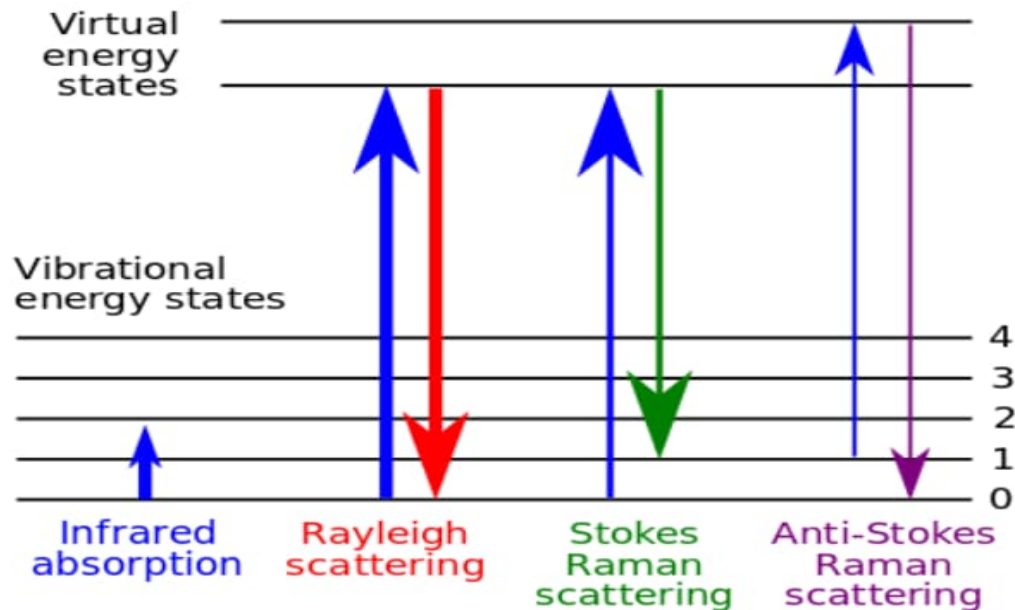
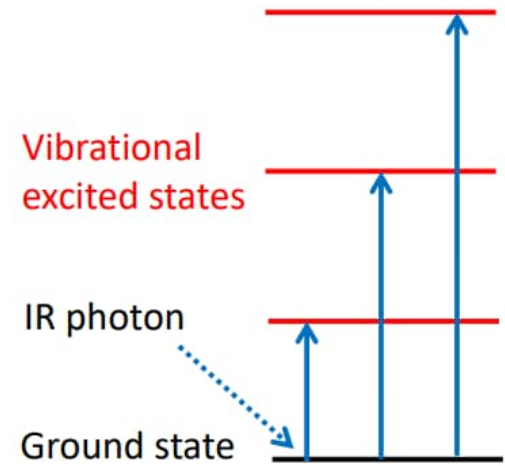


Information gained



Interpretation of Data

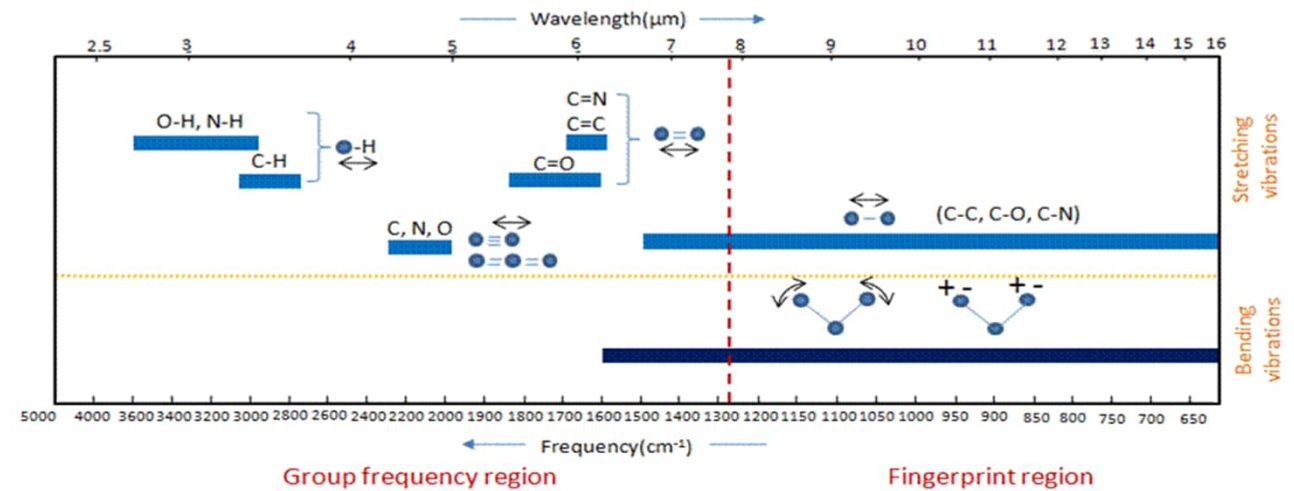
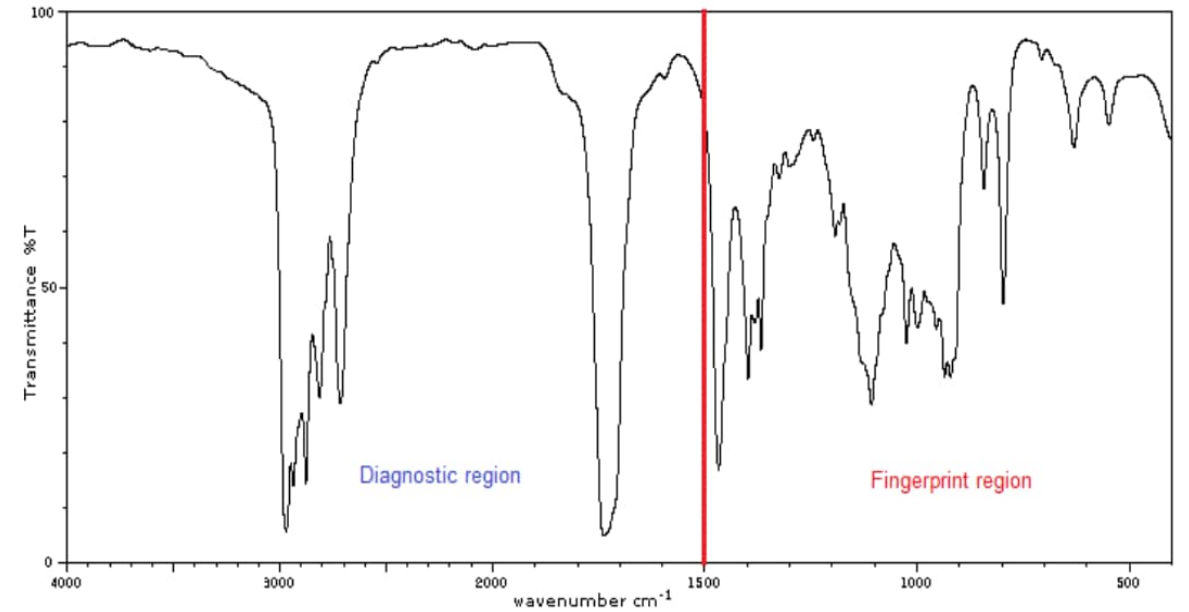
- electronic > vibrational > rotational level
- IR Spectroscopy -> molecule excited with IR radiation
- Net change in dipole moment in a molecule as it vibrates or rotates
- Typical energy range: 40–4000 cm^{-1} (1–100 THz)



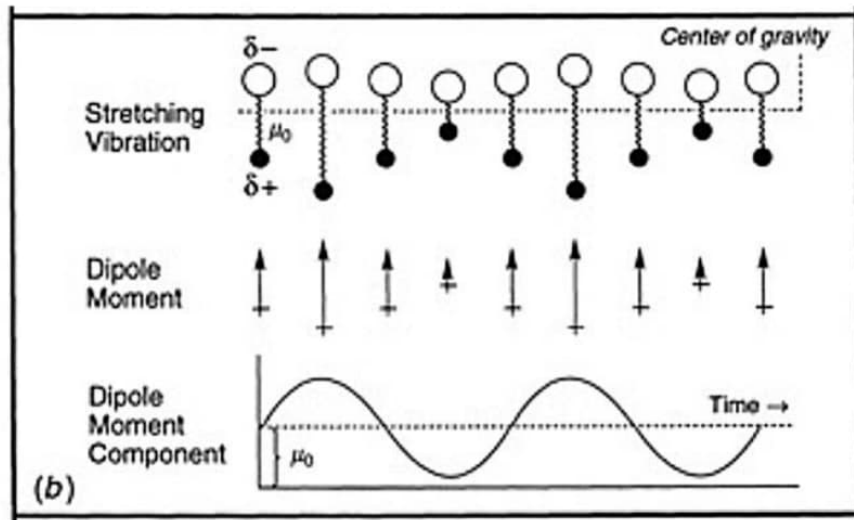
Interpretation of Data

IR spectra can be divided into two main regions:

- Diagnostic region/ Group Frequency Region (4000 to 1600 cm^{-1})
- Fingerprint region (1500 to 700 cm^{-1})



Selection Rules

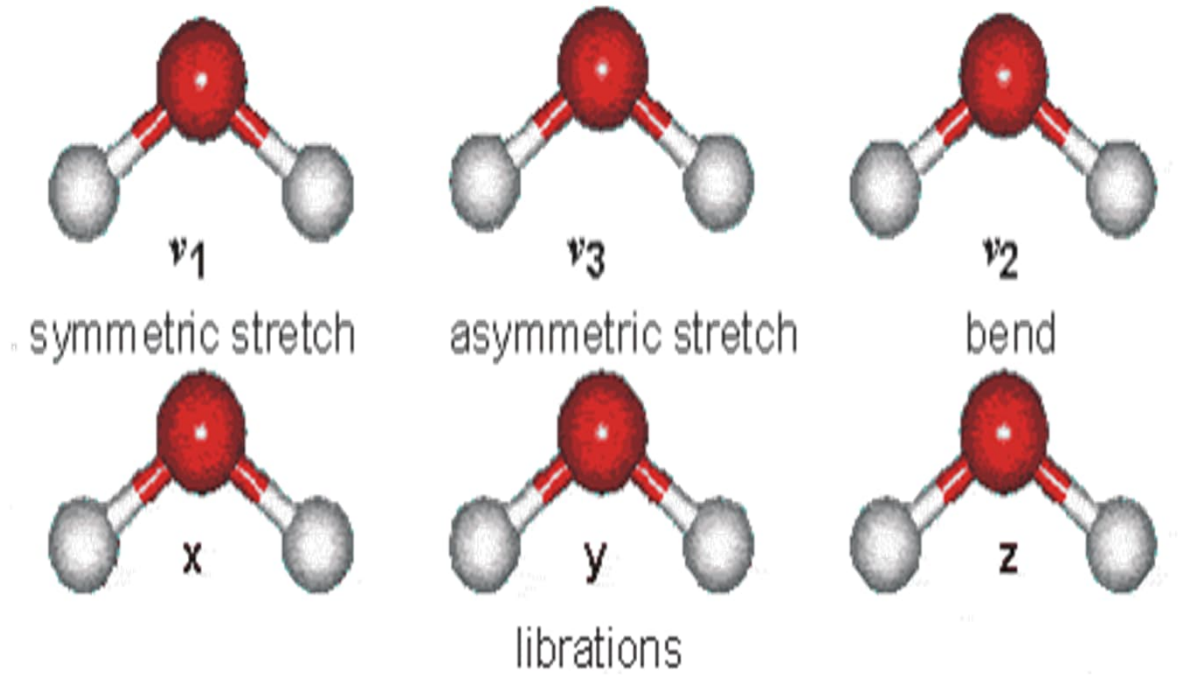
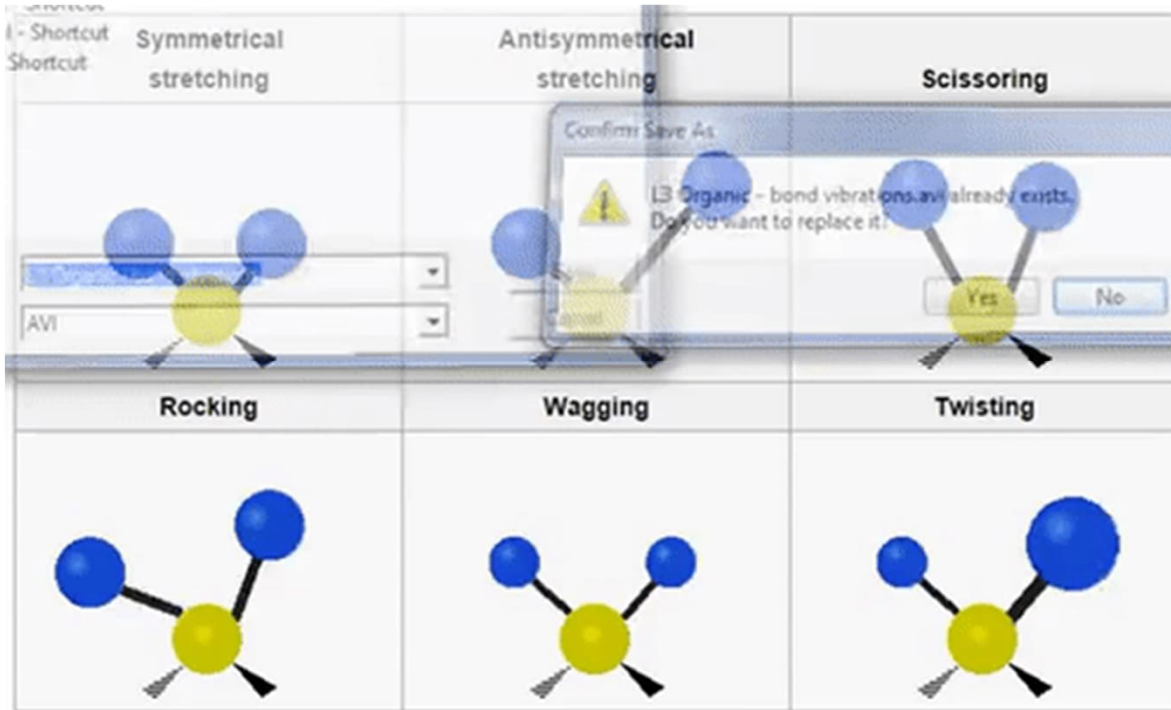


A vibrational mode is IR active if the dipole moment of the system changes
Consequently, centrosymmetric vibrational modes are IR inactive
For example, symmetric C–H stretching of methane (CH_4) is not IR active

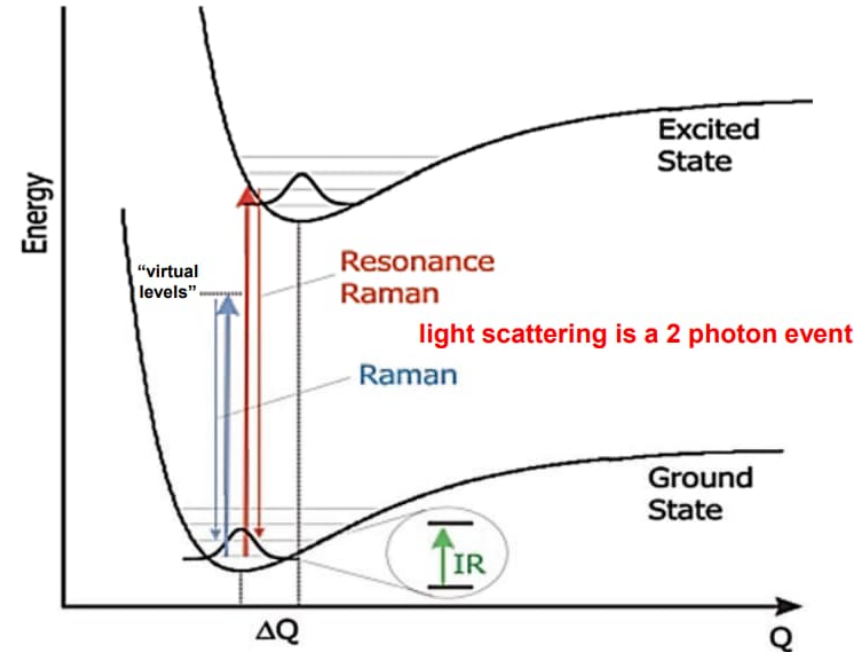
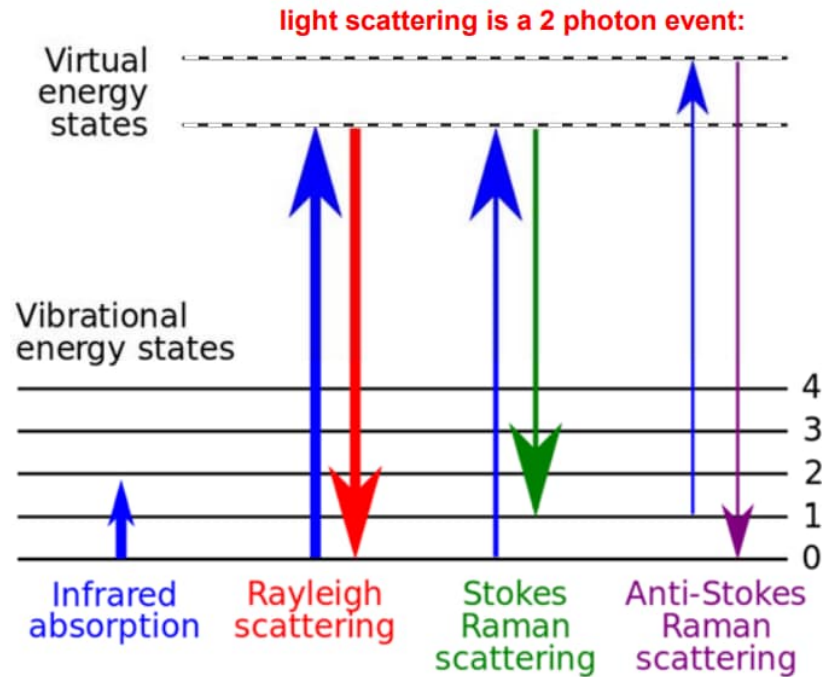
The larger the change of the dipole moment, the higher the intensity.

the vibrational excitation must change.

Vibration Modes



IR vs. Raman

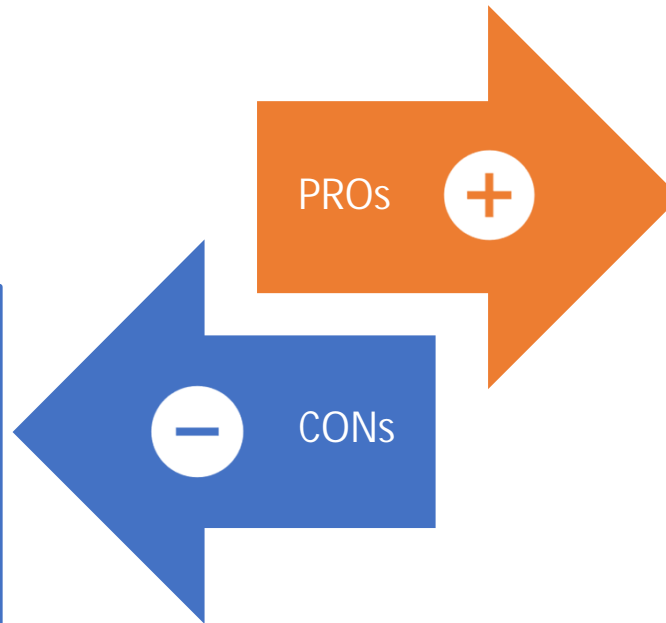


- Infrared absorption
- (1 photon process)
- change the dipole moment of the molecule
- must be x, y, or z symmetry

- Raman Scattering
- 2 photon process
- The polarizability must change
- Raman active modes must go as quadratics (xy, xz, yz, x², y², z²)

Conclusion

- Difficulties in analyzing aqueous solution -> high absorption of water in the infrared region
- Cannot identify molecules comprised of two identical atoms symmetric (e.g., N₂ or O₂)



- It is a non-destructive technique
- It provides a precise measurement
- Sample in any state may be analyzed
- Fast and easy process
- It can increase sensitivity
- Quantitative and qualitative Analysis

Research examples



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Chemistry
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Full Paper

New s-Block Metal Pyridinedicarboxylate Network Structures through Gas-Phase Thin-Film Synthesis

Jenna Penttinen, Mikko Nisula, Prof. Maarit Karppinen ✉

First published: 05 June 2019 | <https://doi.org/10.1002/chem.201901034> | Citations: 13

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COMMUNICATION



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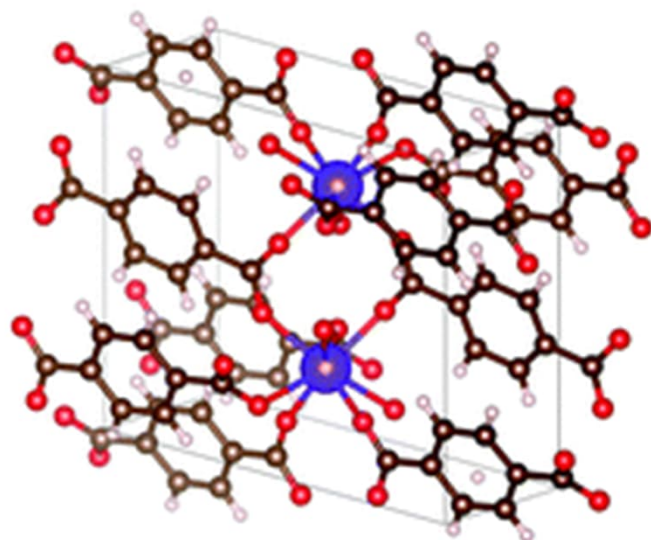
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ALD/MLD synthesis of amorphous MOF thin film
Neodymium Terephthalate thin film
300 cycles (4 s Nd(thd)₃ → 5 s N₂ → 7.5 s TPA → 25 s N₂)
94 nm thick



XRR analysis
Thickness, film density and surface roughness



GIXRD analysis
Crystal structure and crystallinity



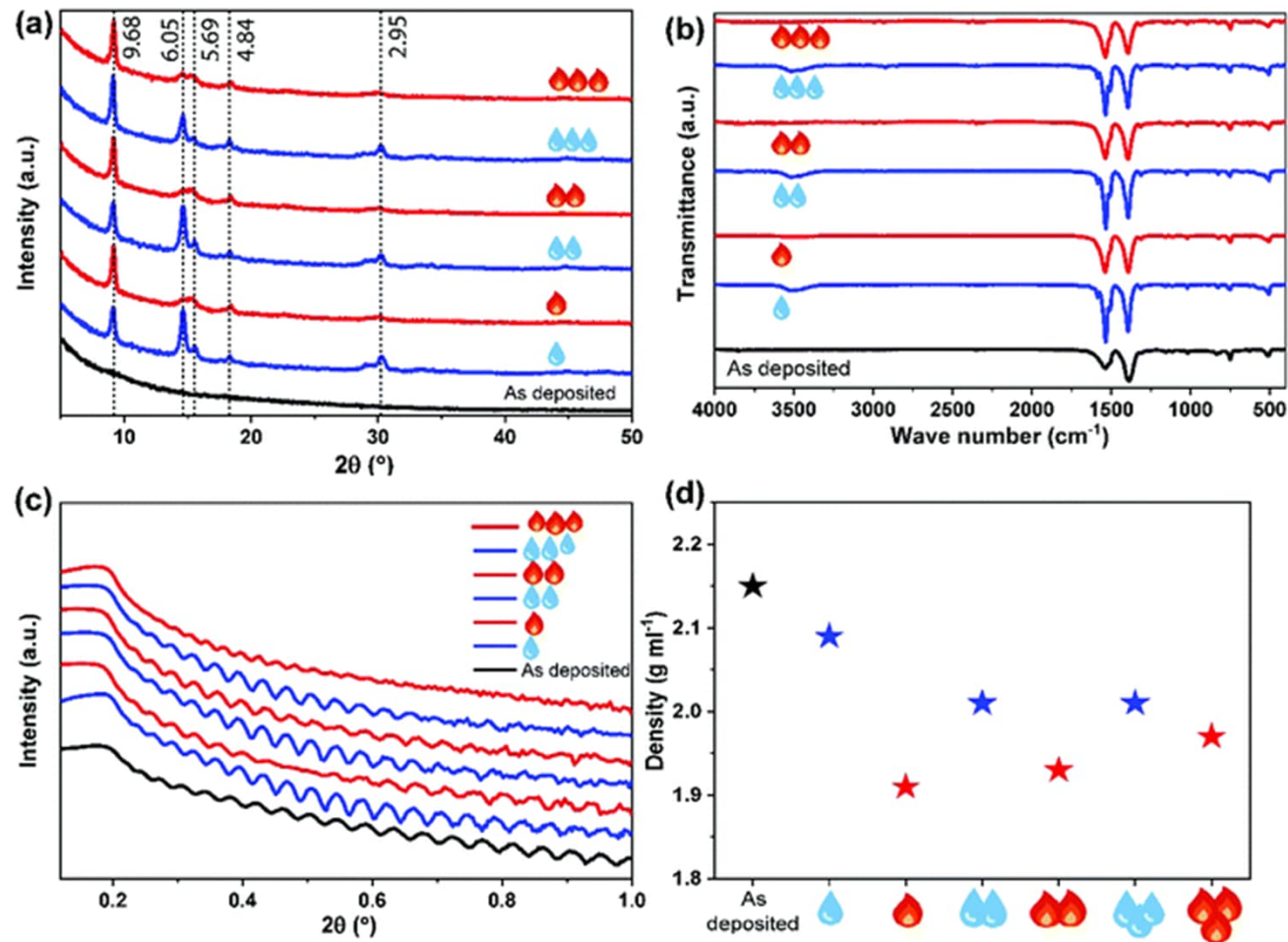
FTIR
Bonding information – bridge bonding of carboxylate groups



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- FTIR confirmed bridging-type mode of carboxylate groups
- Transition from amorphous to crystalline after water absorption
- New crystal phase discovered
- Water removal by heat-treatment but band broadening of FTIR spectrum
- Analysis methods compliment each other



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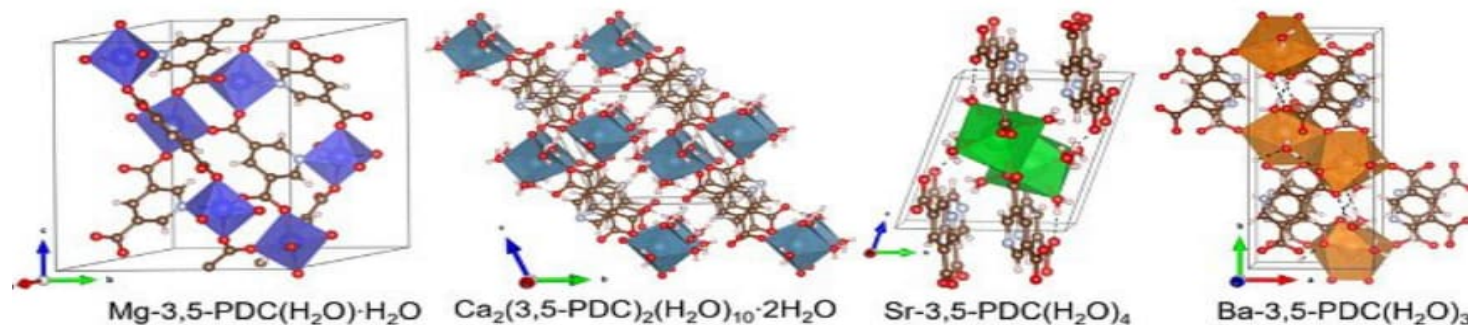
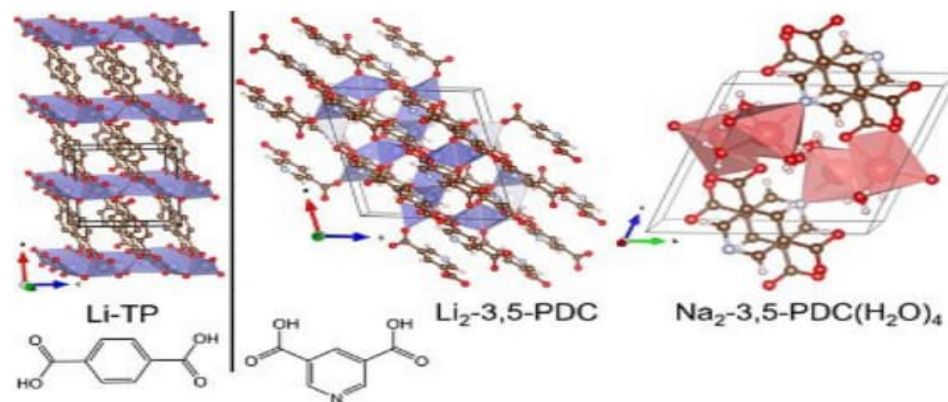
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ALD/ MLD for new metal organic structures:

- crystalline Li-, Na-, and K-based 3,5-pyridinedicarboxylate (3,5-PDC) thin films
- amorphous metal–organic thin films: Mg-, Ca-, Sr-, and Ba-based 3,5-PDC films
- The chemical composition/bonding was studied by FTIR



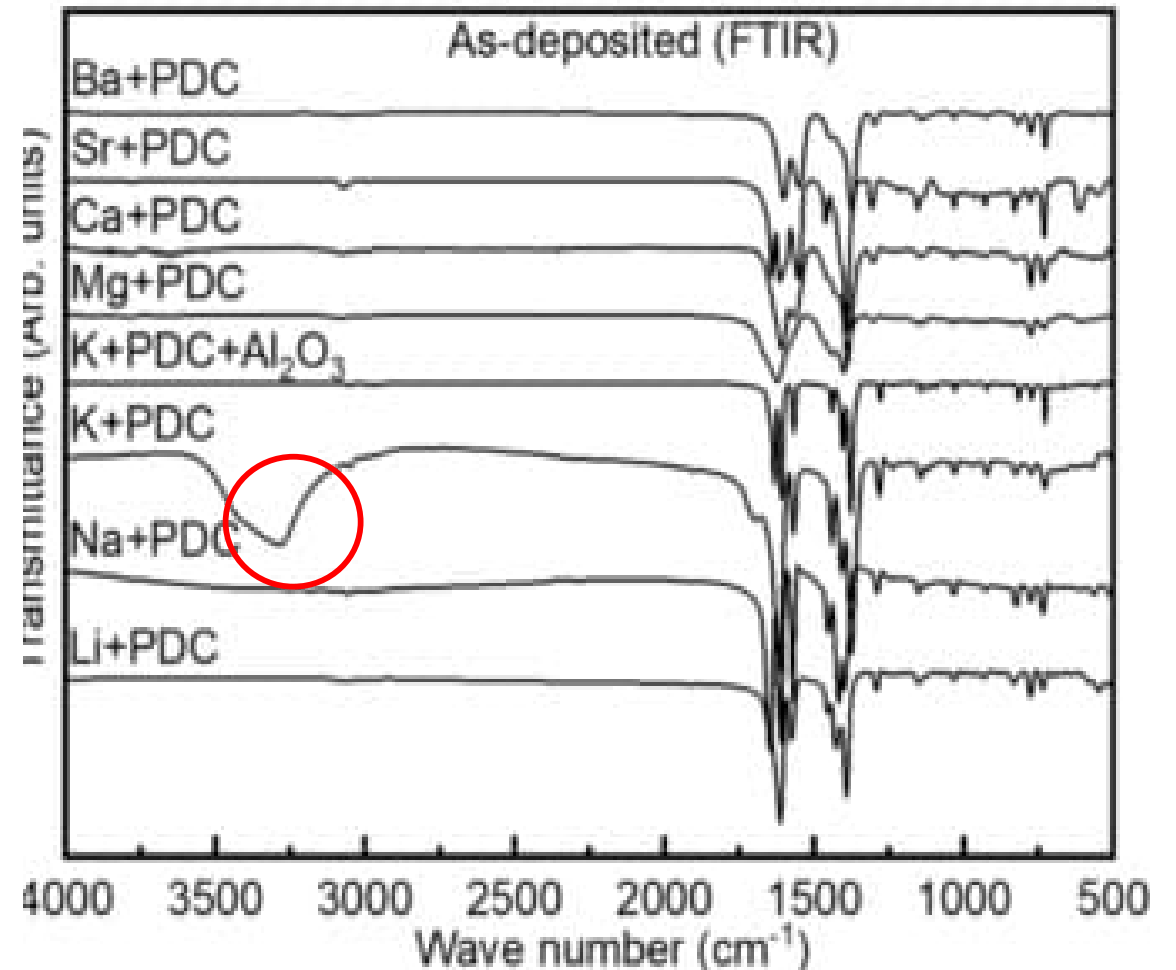


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- K-based film a broad band is seen around 3400 cm^{-1} indicative of incorporated water.
- K+PDC+ Al_2O_3 does not show any indication of absorbed water
- No absorption band around 1700 cm^{-1} -> dicarboxylic acid precursor reacts through hydrogen bonding
- The region around 1720 cm^{-1} lacks the absorption band -> free COOH acid groups
- Absorption bands seen in all the spectra around 1400 and 1600 cm^{-1}
 - asymmetric and symmetric stretching vibrations of the carboxylate group

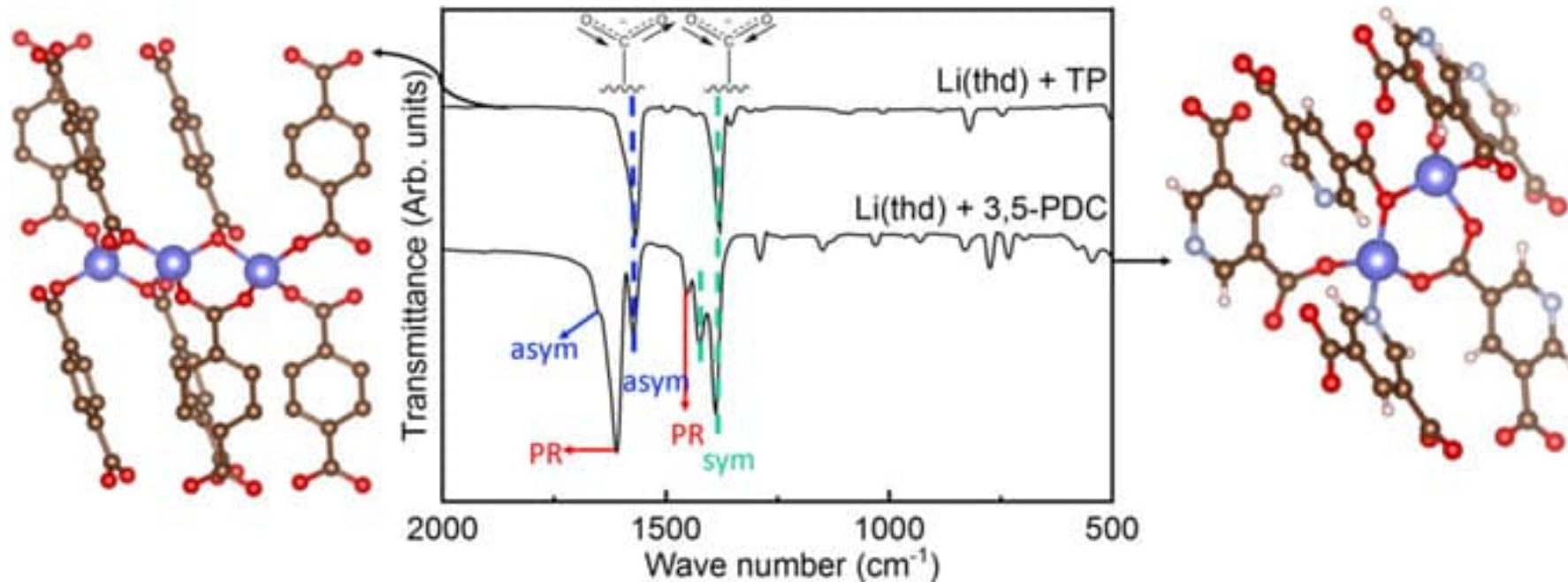




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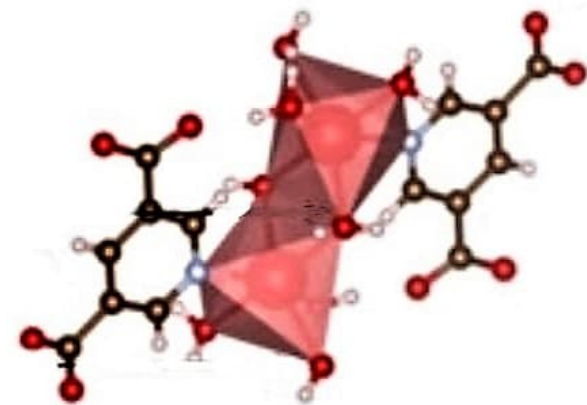
- bridging-type bonding ($\sim 1455 \text{ cm}^{-1}$ and $\sim 1445 \text{ cm}^{-1}$)-> carboxylate peaks
- Confirm the participation of the pyridyl-N entity -> around 1450 cm^{-1}



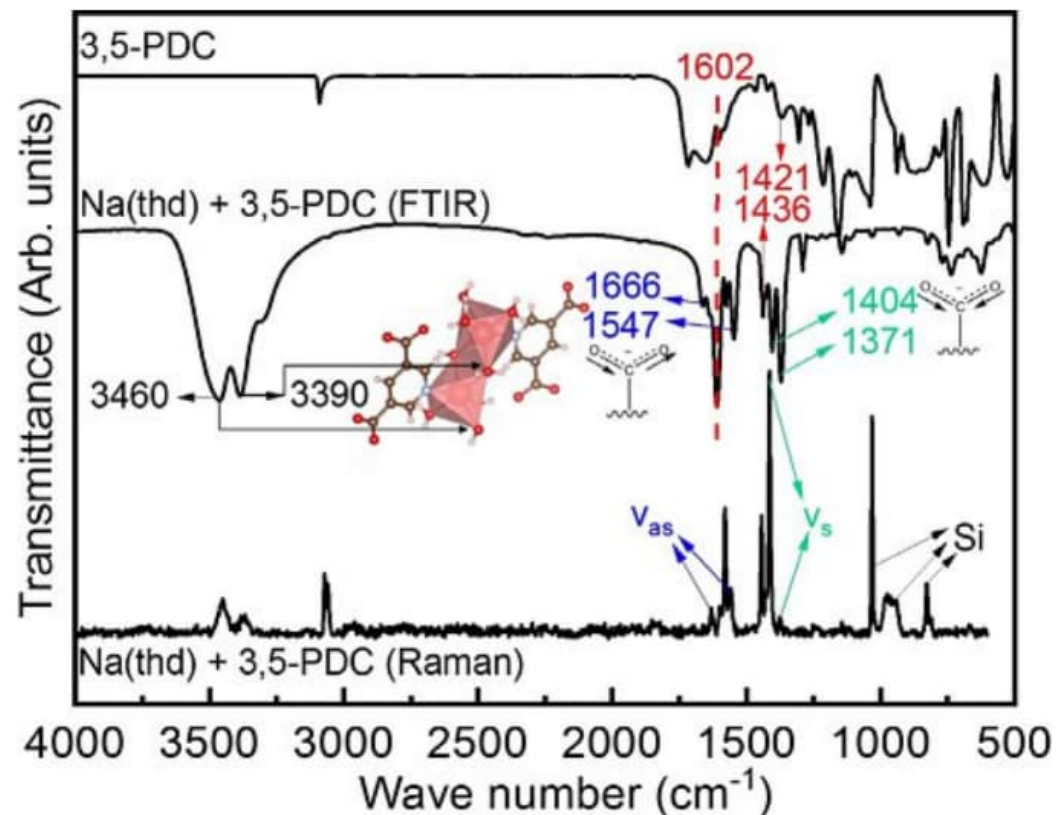
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- Structure of $\text{Na}_2\text{-3,5-PDC}(\text{H}_2\text{O})_4$:
 - Absorption peaks at 3457 and 3390 cm^{-1} are due to the (OH) vibrations.
 - absorption bands at 1547 and 1404 cm^{-1} -> asymmetric and symmetric stretching vibrations of the carboxylate group.
 - Shift in the position of the pyridine-ring (PR) stretching from 1421 cm^{-1} to 1436 cm^{-1} -> pyridine-N coordination to the Na^+ ion
 - PR stretching at 1602 cm^{-1} for both the thin film and the 3,5-PDC precursor.
 - Around 1577 cm^{-1} -> conjugated PR due to the weaker aromaticity of the salt.



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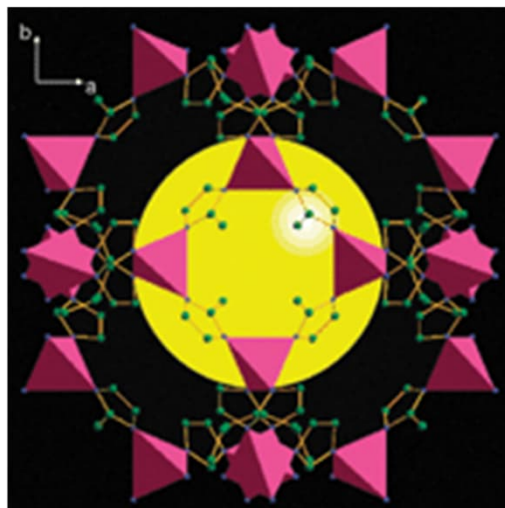


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Zeolitic imidazolate framework
Metal ions bridged by imidazolate units
Nanoporous material



XRD, SEM and BET analysis
Identity, purity and pore size



High pressure *in situ* measurement
39 GPa with diamond anvil cell
Samples 30 μm



FTIR
Micro-spectroscopy system
Structural modification, crystallinity



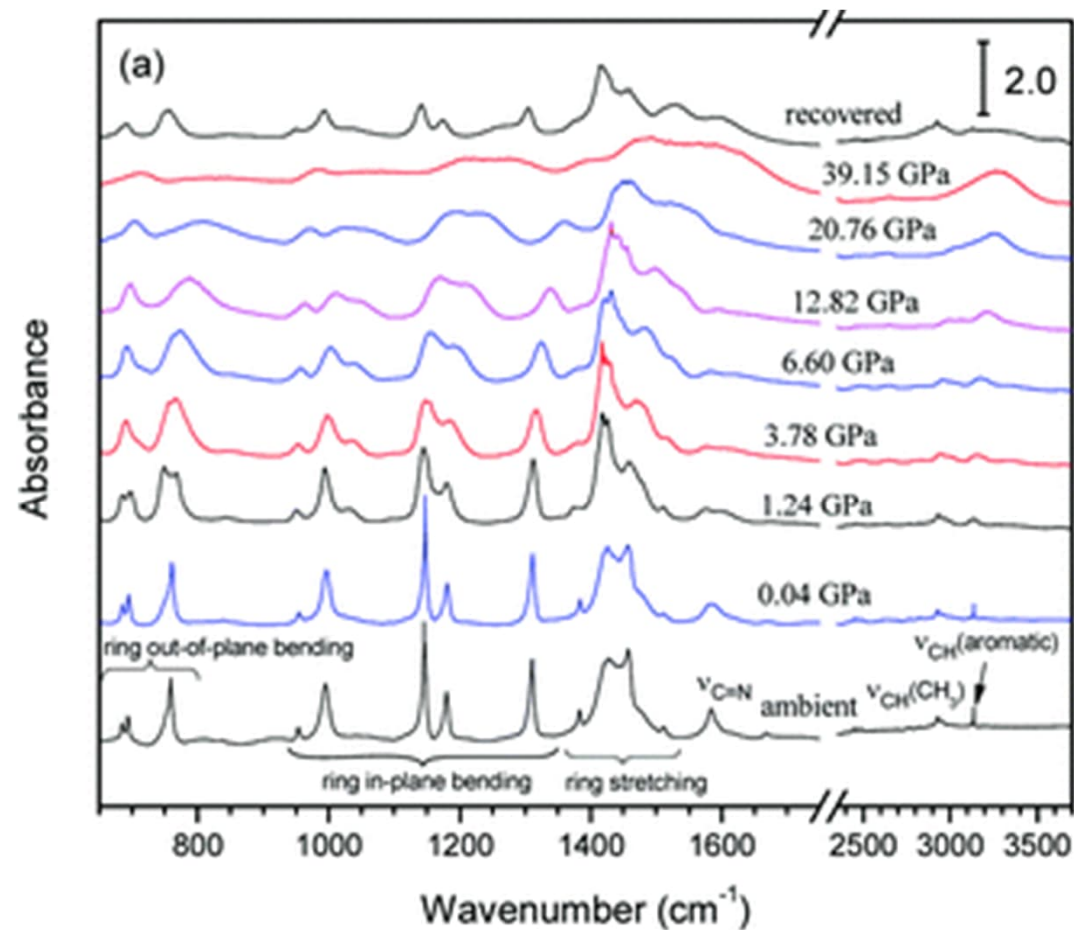
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- Pressure effects of compression up to 1.6 GPa reversible
- Higher pressures result in irreversible structural transitions to disordered or amorphous phase
- *In situ* IR spectroscopy under high pressure conditions



The background is a deep blue gradient with two prominent, wavy bands of glowing white and light blue particles. These particles are arranged in a way that suggests movement and energy, creating a sense of depth and dynamic light. The overall effect is reminiscent of a digital or scientific visualization.

Questions?